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<b>(21) International Application Number:</b> PCT/US98/07316 <b>(22) International Filing Date:</b> 16 April 1998 (16.04.98)  <b>(30) Priority Data:</b> 08/837,503 18 April 1997 (18.04.97) US  <b>(71) Applicant:</b> HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US). <b>(72) Inventor:</b> DOLAN, Shawn, E.; 37934 Utica Road, Sterling Heights, MI 48312 (US). <b>(74) Agent:</b> WISDOM, Norvell, E., Jr.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).		<b>(81) Designated States:</b> AU, BR, CA, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR TOUCHING UP PRETREATED METAL SURFACES  <b>(57) Abstract</b>  Defects in an initial protective coating, particularly a conversion coating, on a metal substrate can be touched up so as to at least equal the original coating in corrosion protection by use of a dry-in-place aqueous acidic liquid comprising: (A) fluorometallate anions; (B) divalent or tetravalent cations of elements selected from the group consisting of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and strontium; (C) a component selected from the group consisting of phosphorus-containing inorganic oxyanions and phosphonate anions; and (D) a component of water-soluble and/or dispersible organic polymers and/or polymer-forming resins.		

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## PROCESS FOR TOUCHING UP PRETREATED METAL SURFACES

### BACKGROUND OF THE INVENTION

This invention relates to processes for treating a metal surface on which a protective coating has previously been formed and remains in place, with its protective qualities intact, on one part of the surface but is totally or partially absent from, or is present only in a damaged condition over, one or more other parts of the surface, so that its protective value in these areas of at least partial damage or absence has been diminished. (Usually the absence or damage of the initial protective coating has been unintentional and has occurred as a result of such events as imperfectly uniform formation of the initial protective coating, mechanical damage of the initial protective coating, spotty exposure of the initially coated surface to solvents for the initial protective coating, or the like.) Particularly if the surface in question is large and the damaged area(s) relatively small, it is often more economical to attempt to create or restore the full protective value of the original coating primarily in only the absent or damaged areas, without completely recoating the object. Such a process is generally known in the art, and will be briefly described herein, as

"touching up" the surface in question. This invention is particularly well suited to touching up surfaces in which the original protective coating is a conversion coating initially formed on a primary metal surface, more particularly a primary metal surface consisting predominantly of iron, aluminum, and/or zinc.

5 A variety of materials have been taught in the prior art for the general purposes of the present invention, but most of if not all of them contain hexavalent chromium, which is environmentally undesirable.

One object of this invention is to avoid any substantial use of hexavalent chromium and other materials such as ferricyanide that have been identified as environmentally damaging. Other concurrent or alternative objects are to achieve at least as good protective  
10 qualities in the touched up areas as in those parts of the touched up surfaces where the initial protective coating is present and undamaged; to avoid any damage to the protective coating from contacting it with the touching up composition; and to provide an economical touching up process. Other objects will be apparent to those skilled in the art from the description below.

Except in the claims and the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated  
20 is generally preferred. Also, unless expressly stated to the contrary: percent, "parts of", and ratio values are all by weight or mass; the term "paint" includes all similar materials that may be described by more specialized terms such as "varnish", "lacquer", "shellac", "base coat", "top coat", and the like; the term "polymer" includes "oligomer", "copolymer", "terpolymer", and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mix-  
25 tures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, or of generation *in situ* within a combination by one or more chemical reactions, as noted in the description, between  
30 other material(s) newly added to the combination and material(s) already present in the combination, and does not necessarily preclude other unspecified chemical interactions

among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole (any counterions thus implicitly specified should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to one of the objects of the invention); any definition of an acronym or other type of abbreviation applies, without the need for repetition of the definition, to all subsequent uses of the same abbreviation and applies, *mutatis mutandis*, to grammatical variations of the original meaning and abbreviation; and the term "mole" and its grammatical variations may be applied to elemental, ionic, and any other chemical species defined by number and type of atoms present, as well as to compounds with well defined molecules.

#### BRIEF SUMMARY OF THE INVENTION

It has been found that excellent touching up quality, particularly for corrosion resistance in combination with a conversion coating, can be achieved by (I) covering the areas to be touched up with a layer of a liquid composition that comprises, preferably consists essentially of, or more preferably consists of, water and:

- (A) a component of fluorometallate anions, each of said anions consisting of (i) at least four fluorine atoms, (ii) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron, and, optionally, one or both of (iii) at least one ionizable hydrogen atom, and (iv) at least one oxygen atom; preferably the anions are fluorotitanate (i.e.,  $\text{TiF}_6^{-2}$ ) or fluorozirconate (i.e.,  $\text{ZrF}_6^{-2}$ ), most preferably fluorotitanate;
- (B) a component of divalent or tetravalent cations of elements selected from the group consisting of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and strontium; preferably, with increasing preference in the order given, at least 60, 70, 80, 90, 95, or 99 % by weight of the total of component (B) consists of cobalt, nickel, manganese, or magnesium, more preferably of manganese, cobalt, or nickel, most preferably of manganese; independently, the ratio of the total number of cations of this component to the total number of anions of component (A) preferably is at least, with increasing preference in the order given, 0.20:1.0, 0.33:1.0, 0.40:1.0, 0.60:1.0, 0.70:1.0, 0.80:1.0, 0.90:1.0, 1.00:1.0, or 1.10:1.0 and

independently preferably is not more than, with increasing preference in the order given, 3:1.0, 2.5:1.0, 2.1:1.0, 1.8:1.0, 1.6:1.0, 1.4:1.0, or 1.20:1.0;

(C) a component of phosphorus-containing inorganic oxyanions and/or phosphonate anions; and

5 (D) a component of water-soluble and/or -dispersible organic polymers and/or polymer-forming resins, preferably in an amount such that the ratio of the solids content of the organic polymers and polymer-forming resins in the composition to the content of component (A) is at least, with increasing preference in the order given, 0.2:1.0, 0.5:1.0, 0.75:1.0, 0.90:1.0, 1.05:1.0, 1.10:1.0, 1.15:1.0, or 1.20:1.0 and  
10 independently preferably is not more than, with increasing preference in the order given, 3.0:1.0, 2.6:1.0, 2.3:1.0, 2.0:1.0, 1.7:1.0, 1.5:1.0, or 1.3:1.0;

and, optionally, one or more of the following components:

(E) an acidifying component that is not part of any of the previously recited components;

15 (F) a component of dissolved oxidizing agent that is not part of any of the previously recited components, preferably a peroxy compound, more preferably hydrogen peroxide;

(G) a component selected from dissolved or dispersed complexes, stabilized against settling, that are not part of any of the previously recited components, said complexes resulting from reaction between (1) a material selected from fluorometal-  
20 late anions, each of said anions consisting of (1.1) at least four fluorine atoms, (1.2) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron, and, optionally, one or both of (1.3) ionizable hydrogen atoms and (1.4) one or more oxygen atoms and  
25 (2) one or more materials selected from the group consisting of metallic and metalloid elements and the oxides, hydroxides, and carbonates of these metallic or metalloid elements, said reaction producing a reaction product that is not part of any of the previously recited components; preferably this component results from reaction of silica or of vanadium(V) oxide as reactant (2); and

30 (H) a viscosity increasing component that is not part of any of the previously recited components,

and then (II) drying into place over the surface the liquid layer formed in step (I).

It should be understood that the components listed need not necessarily all be provided by separate chemicals. For example, it is preferred that the fluorometallate anions and phosphorous containing anions both be added in the form of the corresponding acids, thereby also providing at least some, and usually all, of acidifying component (E).

Various embodiments of the invention include processes for treating surfaces as described above, optionally in combination with other process steps that may be conventional *per se*, such as precleaning, rinsing, and subsequent further protective coatings over those formed according to the invention, and articles of manufacture including surfaces treated according to a process of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

For a variety of reasons, it is preferred that compositions used according to the invention as defined above should be substantially free from many ingredients used in compositions for similar purposes in the prior art. Specifically, it is increasingly preferred in the order given, independently for each preferably minimized component listed below, that these compositions, when directly contacted with metal in a process according to this invention, contain no more than 1.0, 0.35, 0.10, 0.08, 0.04, 0.02, 0.01, 0.001, or 0.0002, percent of each of the following constituents: hexavalent chromium; ferricyanide; ferrocyanide; sulfates and sulfuric acid; anions containing molybdenum or tungsten; alkali metal and ammonium cations; pyrazole compounds; sugars; gluconic acid and its salts; glycerine;  $\alpha$ -glucoheptanoic acid and its salts; and myoinositol phosphate esters and salts thereof.

Component (C) as defined above is to be understood as including all of the following inorganic acids and their salts that may be present in the composition: hypophosphorous acid ( $H_3PO_2$ ), orthophosphorous acid ( $H_3PO_3$ ), pyrophosphoric acid ( $H_4P_2O_7$ ), orthophosphoric acid ( $H_3PO_4$ ), tripolyphosphoric acid ( $H_5P_3O_{10}$ ), and further condensed phosphoric acids having the formula  $H_{x+2}P_xO_{3x+1}$ , where  $x$  is a positive integer greater than 3. Component (C) also includes all phosphonic acids and their salts.

Generally, inorganic phosphates, particularly orthophosphates, phosphites, hypophosphites, and/or pyrophosphates, especially orthophosphates, are preferred for component (C) because they are more economical. Phosphonates are also suitable and may be advantageous for use with very hard water, because the phosphonates are more effective

chelating agents for calcium ions. Acids and their salts in which phosphorous has a valence less than five may be less stable than the others to oxidizing agents and are less preferred in compositions according to the invention that are to contain oxidizing agents.

Component (D) is preferably selected from the group consisting of epoxy resins, aminoplast (i.e., melamine-formaldehyde and urea-formaldehyde) resins, tannins, phenol-formaldehyde resins, and polymers of vinyl phenol with sufficient amounts of alkyl- and substituted alkyl-aminomethyl substituents on the phenolic rings to render the polymer water soluble or dispersible. More preferably, component (D) is selected from epoxy resins and/or, most preferably only from, polymers and/or copolymers of one or more  $y$ -(N-R<sup>1</sup>-N-R<sup>2</sup>-aminomethyl)-4-hydroxy-styrenes, where  $y = 2, 3, 5, \text{ or } 6$ , R<sup>1</sup> represents an alkyl group containing from 1 to 4 carbon atoms, preferably a methyl group, and R<sup>2</sup> represents a substituent group conforming to the general formula  $H(CHOH)_nCH_2-$ , where  $n$  is an integer from 1 to 7, preferably from 3 to 5. The average molecular weight of these polymers preferably is within the range from 700 to 70,000, or more preferably from 3,000 to 20,000.

The pH of a composition used according to the invention preferably is at least, with increasing preference in the order given, 0.5, 1.0, 1.3, 1.5, 1.7, 1.90, 2.00, 2.10, 2.20, 2.30, or 2.40 and independently preferably is not more than, with increasing preference in the order given, 5.0, 4.5, 4.0, 3.7, 3.5, 3.3, 3.1, 2.9, 2.70, or 2.60.

If used, component (F) preferably is present in a working composition according to this invention in an amount sufficient to provide a concentration of oxidizing equivalents per liter of composition that is equal to that of a composition containing from 0.5 to 15, or more preferably from 1.0 to 9.0 % of hydrogen peroxide. (The term "oxidizing equivalent" as used herein is to be understood as equal to the number of grams of oxidizing agent divided by the equivalent weight in grams of the oxidizing agent. The equivalent weight of the oxidizing agent is the gram molecular weight of the agent divided by the change in valency of all atoms in the molecule which change valence when the molecule acts as an oxidizing agent; usually, this is only one element, such as oxygen in hydrogen peroxide.)

The term "stabilized against settling" in the description of component (G) above means that the composition containing the material does not suffer any visually detectable



settling or separation into distinct liquid phases when stored for a period of 100, or more preferably 1000, hours at 25° C. Materials for component (G) may be prepared by adding one or more metallic and/or metalloid elements or their oxides, hydroxides, and/or carbonates to an aqueous composition containing one or more substances that, if left unreacted, could become part of component (A). A spontaneous chemical reaction normally ensues, converting the added element, oxide, hydroxide, or carbonate into a soluble species. The reaction to form this soluble species can be accelerated by use of heat and stirring or other agitation of the composition. The formation of the soluble species is also aided by the presence in the composition of suitable complexing ligands, such as peroxide and fluoride. Preferably the amount of component (G) when used in a concentrate composition is not greater than that formed by addition, with increasing preference in the order given, of up to 50, 20, 12, 8, 5, or 4 parts per thousand, based on the ultimate total mass of the concentrate composition, of the metallic or metalloid element or its stoichiometric equivalent in an oxide, hydroxide, or carbonate, to the concentrate composition. Independently, the amount of component (G) when used in a concentrate composition preferably is at least as great as that formed by addition, with increasing preference in the order given, of at least 0.1, 0.20, 0.50, or 1.0 parts per thousand, based on the ultimate total mass of the concentrate composition, of the metallic or metalloid element or its stoichiometric equivalent in an oxide, hydroxide, or carbonate, to the concentrate composition.

The effectiveness of a treatment according to the invention appears to depend predominantly on the total amounts of the active ingredients that are dried in place on each unit area of the treated surface, and on the nature and ratios of the active ingredients to one another, rather than on the concentration of the acidic aqueous composition used, and the speed of drying has not been observed to have any technical effect on the invention, although it may well be important for economic reasons. If practical in view of the size of the object treated and of the size of the areas touched up, drying may be speeded by placement in an oven, use of radiative or microwave heating, or the like. If speed of treatment is desired, but placing the entire object in an oven is inconvenient, a portable source of hot air or radiation may be used in the touched up area(s) only. If ample time is available at acceptable economic cost, a liquid film applied according to this invention may simply be allowed to dry spontaneously in the ambient atmosphere with equally good re-

sults insofar as the protective quality of the coating is concerned. Suitable methods for each circumstance will be readily apparent to those skilled in the art.

As a general guide, it is normally preferable, independently for each concentration and ratio stated and with increasing preference in the order given for each number sequence, if the working composition has: a concentration of at least 0.010, 0.020, 0.030, 0.040, 0.045, 0.050, 0.055, or 0.060 gram moles per kilogram of total composition (hereinafter usually abbreviated as "M/kg") of fluorometallate anions component (A); at least 0.015, 0.025, 0.030, 0.035, 0.040, 0.045, 0.050, 0.055, 0.060, 0.064, or 0.067 M/kg of phosphorus from component (C); a ratio of the concentration of phosphorus from component (C) in M/kg to the concentration of fluorometallate anions from component (A) in M/kg that is at least 0.12:1.0, 0.25:1.0, 0.35:1.0, 0.45:1.0, 0.55:1.0, 0.65:1.0, 0.75:1.0, 0.85:1.0, 0.95:1.0, 1.00:1.0, 1.05:1.0, or 1.10:1.0 and independently preferably is not more than 5.0:1.0, 4.0:1.0, 3.5:1.0, 3.0:1.0, 2.5:1.0, 2.0:1.0, 1.8:1.0, 1.6:1.0, 1.50:1.0, 1.40:1.0, 1.30:1.0, 1.25:1.0, 1.20:1.0, or 1.15:1.0; and at least 0.10, 0.20, 0.30, 0.40, 0.60, 0.80, 1.00, or 1.20 % of solids from component (D). Working compositions containing up to at least five times these amounts of active ingredients are also fully satisfactory to use. Dilute compositions, within these preferred ranges, that include the necessary active ingredients (A) through (D) only may have inadequate viscosity to be self-supporting in the desired thickness for touching up areas that can not be placed in a substantially horizontal position during treatment and drying; if so, one of the materials known in the art, such as natural gums, synthetic polymers, colloidal solids, or the like should be used as optional component (H), as generally known in the art, unless sufficient viscosity is provided by one or more of other optional components of the composition.

A working composition according to the invention may be applied to a metal workpiece and dried thereon by any convenient method, several of which will be readily apparent to those skilled in the art. For example, coating the metal with a liquid film may be accomplished by immersing the surface in a container of the liquid composition, spraying the composition on the surface, coating the surface by passing it between upper and lower rollers with the lower roller immersed in a container of the liquid composition, contact with a brush or felt saturated with the liquid treatment composition, and the like, or by a mixture of methods. Excessive amounts of the liquid composition that might other-

wise remain on the surface prior to drying may be removed before drying by any convenient method, such as drainage under the influence of gravity, passing between rolls, and the like. The temperature during application of the liquid composition may be any temperature within the liquid range of the composition, although for convenience and economy in application, normal room temperature, i.e., from 20 - 27 ° C, is usually preferred.

Preferably the amount of composition applied in a process according to this invention is chosen so as to result, after drying into place, in at least as good corrosion resistance for the parts of the surface treated according to the invention as in the parts of the same surface where the initial protective coating is present and a process according to the invention has not been applied. Ordinarily, for most common protective phosphate and chromate conversion coatings as initial protective coatings, such protection will be achieved if the total add-on mass (after drying) of the coating applied in a process according to the invention is at least, with increasing preference in the order given, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, or 0.60 grams per square meter of surface coated (hereinafter usually abbreviated as "g/m<sup>2</sup>"). Independently, at least equal corrosion resistance ordinarily will be achieved even if the add-on mass is not, and therefore for reasons of economy the add-on mass preferably is not, greater than, with increasing preference in the order given, 4.0, 3.0, 2.0, 1.7, 1.4, 1.2, 1.0, 0.90, 0.85, 0.80, or 0.75 g/m<sup>2</sup>.

The add-on mass of the protective film formed by a process according to the invention may be conveniently monitored and controlled by measuring the add-on weight or mass of the metal atoms in the anions of component (A) as defined above, except in the unusual instances when the initial protective coating and/or the underlying metal substrate contains the same metal element(s). The amount of these metal atoms may be measured by any of several conventional analytical techniques known to those skilled in the art. The most reliable measurements generally involve dissolving the coating from a known area of coated substrate and determining the content of the metal of interest in the resulting solution. The total add-on mass can then be calculated from the known relationship between the amount of the metal in component (A) and the total mass of the part of the total composition that remains after drying. However, this method is often impractical for use with this invention, because the area touched up is not always precisely defined. A more prac-

tical alternative is generally provided by small area X-ray spectrographs that, after conventional calibration, directly measure the amount(s) per unit area of individual metallic element(s) present in a coating, free from almost all interferences except the same elements present in other coatings on, or in a thin layer near the surface of, the underlying metal surface itself.

In many instances sufficiently precise control of the amount of coating used can be determined visually from the color of the area coated, because most preferred compositions for use according to the invention are fairly strongly colored. Unless the surface to be treated happens to be the same or a similar color, the amount of active ingredients can therefore be estimated by the intensity of the color of the liquid film formed in a process according to the invention.

Preferably, the surface to be treated according to the invention is first cleaned of any contaminants, particularly organic contaminants and foreign metal fines and/or inclusions. Such cleaning may be accomplished by methods known to those skilled in the art and adapted to the particular type of substrate to be treated. For example, for galvanized steel surfaces, the substrate is most preferably cleaned with a conventional hot alkaline cleaner, then rinsed with hot water and dried. For aluminum, the surface to be treated most preferably is first contacted with a conventional hot alkaline cleaner, then rinsed in hot water, then, optionally, contacted with a neutralizing acid rinse and/or deoxidized, before being contacted with an acid aqueous composition as described above. Ordinarily, cleaning methods suitable for the underlying metals will also be satisfactory for any part of the initial protective coating that is also coated in a process according to the invention, but care should be taken to choose a cleaning method and composition that do not themselves damage the protective qualities of the initial protective coating in areas that are not to be touched up. If the initial protective coating is thick enough, the surface can be satisfactorily cleaned by physically abrading, as with sandpaper or another coated abrasive, the area(s) to be touched up and any desired overlap zone, where the initial protective coating is still in place, around the damaged areas to be touched up, then removing the swarf by blowing, brushing, rinsing, or attachment to a cleaning tool, such as a moist cloth.

Usually, it is preferable, as a precaution during a touch up process according to the invention, to apply the composition used for touching up not only to obviously bare

metal or obviously damaged areas of the initial protective coating, but also over a transition or overlap zone of apparently undamaged initial protective coating adjacent to such areas that obviously need touching up. With increasing preference in the order given, such a transition zone has a width that is at least 0.2, 0.5, 0.7, 1.0, 1.5, or 2.0 millimeters and independently preferably, primarily for reasons of economy, is not more than, with increasing preference in the order given, 25, 20, 15, 10, 8, 6, 5, or 3 millimeters.

Virtually any kind of initial protective coating can be touched up effectively for many purposes by a process according to this invention. In particular, but without limitation, conversion coatings produced on underlying metal according to the teachings of any one of the following U. S. Patents, the disclosures of all of which, except to any extent that they may be inconsistent with any explicit statement herein, are hereby incorporated herein by reference, may be effectively touched up by a process according to this invention: 5,595,611 of Jan. 21, 1997 to Boulos et al.; 5,551,994 of Sep. 3, 1996 to Schriever; 5,534,082 of July 9, 1996 to Dollman et al.; 5,507,084 of Apr. 16, 1996 to Ogino et al.; 5,498,759 of March 12, 1996 to Nakada et al.; 5,498,300 of March 12, 1996 to Aoki et al.; 5,487,949 of Jan. 30, 1996 to Schriever; 5,472,524 of Dec. 5, 1995; 5,472,522 of Dec. 5, 1995 to Kawaguchi et al.; 5,452,884 of Oct. 3, 1995; 5,451,271 of Sep. 19, 1995 to Yoshida et al.; 5,449,415 of Sep. 19, 1995 to Dolan; 5,449,414 of Sep. 12, 1995 to Dolan; 5,427,632 of June 27, 1995 to Dolan; 5,415,687 of May 16, 1995 to Schriever; 5,411,606 of May 2, 1995 to Schriever; 5,399,209 of March 21, 1995 to Suda et al.; 5,395,655 of March 7, 1995 to Kazuyuki et al.; 5,391,239 of Feb. 21, 1995 to Boulos; 5,378,392 of Jan. 3, 1995 to Miller et al.; 5,366,567 of Nov. 22, 1994 to Ogino et al.; 5,356,490 of Oct. 18, 1994 to Dolan et al.; 5,342,556 of Aug. 30, 1994 to Dolan; 5,318,640 of June 7, 1994 to Ishii et al.; 5,298,092 of March 29, 1994 to Schriever; 5,281,282 of Jan 25, 1994 to Dolan et al.; 5,268,042 of Dec. 7, 1993 to Carlson; 5,261,973 of Nov. 16, 1993 to Sienkowski et al.; 5,242,714 of Sep. 7, 1993 to Steele et al.; 5,143,562 of Sep. 1, 1992 to Boulos; 5,141,575 of Aug. 25, 1992 to Yoshitake et al.; 5,125,989 of June 30, 1992 to Hallman; 5,091,023 of Feb. 25, 1992 to Saeki et al.; 5,089,064 of Feb. 18, 1992 to Reghi; 5,082,511 of June 21, 1992 to Farina et al.; 5,073,196 of Dec. 17, 1991; 5,045,130 of Sep. 3, 1991 to Gosset et al.; 5,000,799 of March 19, 1991 to Miyawaki; 4,992,196 of Feb. 13, 1991 to Hallman; 4,985,087 of Jan.

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The practice of this invention may be further appreciated by consideration of the following, non-limiting, working examples.

The ingredients in the compositions are given in Table 1. The solution of polymer of substituted vinyl phenol used was made according to the directions of column 11 lines 39 - 52 of U. S. Patent 4,963,596, except that in the final dilution an amount of ortho-phosphoric acid equal to a final concentration of 0.3 %  $H_3PO_4$  was used in addition to the deionized water described in the patent. The solution contained 10 % of the solid polymer. This solution is identified below as "Aminomethyl substituted polyvinyl phenol solution". Composition 1 was prepared generally by adding the acidic ingredients to most of the "other deionized water" shown, then dissolving the manganese(II) oxide, which reacts to yield manganese phosphates and water, then adding the solution of the organic film forming component, and finally adding enough deionized water to bring the total parts to 1000. Composition 2 was made by diluting Composition 1 with deionized water in an amount so that Composition 2 contained 20 % of each of the ingredients other than water in Composition 1.

Table 1

Ingredient	Concentration in Parts of Ingredient in Composition Number:	
	1	2
60 % $H_2TiF_6$ in water	82	16
75 % $H_3PO_4$ in water	45	8.9
Manganese(II) oxide (i.e., $MnO$ )	24	4.8
Aminomethyl substituted polyvinyl phenol solution	602	120
Other deionized water	347	851

Conventional rectangular sheet test pieces of Type 2024-T3 aluminum were pro-

vided with an initial protective coating by subjecting them to the process steps shown in Table 2 below in the order shown in the Table. Contact between the substrate and the liquid composition used in each operation, except for the drying step, was by immersion.

All products identified by trademarks in Table 2 are available commercially from the Henkel Surface Technologies division of Henkel Corp., Madison Heights, Michigan.

TABLE 2

Operation Name	Process Conditions		
	Composition	° C	Contact Time, Minutes
Cleaning	15 grams of RIDOLINE® 53 Cleaner concentrate per liter of cleaning solution; balance water	60	5
Rinsing	Tap water	18 - 23	1
Deoxidizing	DEOXIDIZER™ 6-16 products, used according to manufacturer's directions	18 - 23	3
Rinsing	Tap water	18 - 23	1
Chromate Conversion Coating	ALODINE® 600 products, used according to manufacturer's directions	18 - 23	3
Rinsing	Deionized water	18 - 23	1
Drying	Ambient air	18 - 23	5 - 20

Test substrates prepared in this manner, as long as the coating formed by the above stated process sequence was in place and intact, passed bare salt spray tests for two weeks without evidence of corrosion. However, if the coating was scribed through on, or otherwise mechanically removed from, a portion of the surface, rapid severe pitting of the metal underlying the damaged portions of the coating occurred in salt spray testing.

Substrates for testing in this invention were prepared by scribing through a portion of the coating and/or abrading a portion of the coating with a lofty coated abrasive product (SCOTCH-BRITE™ from Minnesota Mining & Manufacturing Co.), in either instance so as to expose underlying metal on part of the surface of a coated test piece, while

leaving most of the initial coating intact. The area(s) of metal thus exposed, along with a zone two to ten millimeters wide of the intact original coating around each damaged area, were covered with a layer of Composition 1 or 2 as specified in Table 1. The layer of liquid Composition 1 or 2 was sufficiently thick to form a substantially level surface over both the areas of the substrate from which the initial coating had been removed and a two to ten centimeters wide overlap zone around these areas. This layer of liquid composition was then dried into place, usually without applying any heat source but simply preserving the coating in place by orienting the coated sample so that the coating would not run off under the influence of natural gravity until the coating had dried by evaporation of a sufficient fraction of its water content. In some instances, however, drying was accelerated and completed within a few minutes by use of a supply of heated air such as that furnished by a hair dryer or similar appliance. In all instances, the resistance to salt spray corrosion after all of the removed and/or damaged areas had been covered was at least as high as that of an undamaged sample with the initially applied coating intact over all of its surface.

The invention claimed is:

1. A process for touching up a surface of an object, said surface comprising (i) at least one first area of an initial protective coating over an underlying metal substrate, in which said first area the initial protective coating retains all the protective qualities that it had when initially applied and (ii) at least one second area which consists of one or both of (ii.1) an area of exposed metal and (ii) an area of a covering that provides protective qualities inferior to those provided by the initial protective coating in said first area, said process comprising steps of:
- (I) coating at least said second area of said surface to be touched up with a substantially uniform coating of an aqueous liquid composition comprising water and:
- (A) a concentration of a component of fluorometallate anions, each of said anions consisting of: (i) at least four fluorine atoms and (ii) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron; and, optionally, one or both of (iii) at least one ionizable hydrogen atom, and (iv) at least one oxygen atom;
- (B) a concentration of a component of divalent or tetravalent cations of elements selected from the group consisting of cobalt, magnesium, manganese, zinc, nickel, tin, copper, zirconium, iron, and strontium;
- (C) a concentration of a component selected from the group consisting of phosphorus-containing inorganic oxyanions and phosphonate anions; and
- (D) a concentration of a component of water-soluble and/or -dispersible organic polymers and/or polymer-forming resins;
- and
- (II) drying into place on the surface of the object the coating applied in step (I), without intermediate rinsing.
2. A process according to claim 1, wherein, in the liquid composition coated in step (I): the concentration of component (A) is at least about 0.010 M/kg; the concentration of component (B) in M/kg has a ratio to the concentration of component (A) in M/kg that is at least about 0.20:1.0 but not greater than about 3:1.0; the concentration of component (C) is at least about 0.015 M/kg; and the concentration of component (D) is at least about 0.10 %.

3. A process according to claim 2, wherein, in the liquid composition coated in step (I): component (A) is selected from fluorotitanate and fluorozirconate anions; the concentration of component (A) is at least about 0.020 M/kg; at least 60 % of component (B) is selected from the group consisting of cobalt, nickel, manganese, and magnesium; the concentration of component (B) in M/kg has a ratio to the concentration of component (A) in M/kg that is at least about 0.33:1.0 but not greater than about 2.5:1.0; component (C) is selected from orthophosphate, phosphite, hypophosphite, phosphonate and pyrophosphate anions; the concentration of component (C) is at least about 0.030 M/kg; component (D) is selected from the group consisting of epoxy resins, aminoplast resins, tannins, phenol-formaldehyde resins, and polymers of vinyl phenols with alkyl- and/or substituted alkyl-aminomethyl substituents on the phenolic rings, said polymers being water soluble or dispersible to an extent of at least 1 %; the concentration of component (D) in percent of the total composition has a ratio to the concentration of component (A) in percent of the total composition that is from about 0.5:1.0 to about 3:1.0; and the concentration of component (D) is at least about 0.20 %.

4. A process according to claim 3, wherein, in the liquid composition coated in step (I): the concentration of component (A) is at least about 0.025 M/kg; component (B) is selected from the group consisting of cobalt, nickel, and manganese; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is at least about 0.33:1.0 but not greater than about 1.6:1.0; the concentration of component (C) is at least about 0.035 M/kg; component (D) is selected from the group consisting of epoxy resins and polymers and copolymers of one or more  $\gamma$ -(N-R<sup>1</sup>-N-R<sup>2</sup>-aminomethyl)-4-hydroxy-styrenes, where  $\gamma$  = 2, 3, 5, or 6, R<sup>1</sup> represents an alkyl group containing from 1 to 4 carbon atoms, and R<sup>2</sup> represents a substituent group conforming to the general formula H(CHOH)<sub>n</sub>CH<sub>2</sub>-, where n is an integer from 1 to 7, these substituted styrene polymers having an average molecular weight within the range from 700 to 70,000; the ratio of the solids content of the organic polymers and polymer-forming resins in percent by weight of the total composition to the solids content of component (A) in percent by weight of the total composition is within a range from about 0.75:1.0 to 1.9:1.0; and the concentration of component (D) is at least about 0.30 % of the total composition.

5. A process according to claim 4, wherein, in the liquid composition coated in step

(I): the concentration of component (A) is at least about 0.030 M/kg; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is at least about 0.40:1.0 but not greater than about 1.4:1.0; the concentration of component (C) is at least about 0.045 M/kg; component (D) is selected from the group consisting of polymers and copolymers of one or more  $\gamma$ -(N-R<sup>1</sup>-N-R<sup>2</sup>-aminomethyl)-4-hydroxy-styrenes, where  $\gamma$  = 2, 3, 5, or 6, R<sup>1</sup> represents a methyl group, and R<sup>2</sup> represents a substituent group conforming to the general formula H(CHOH)<sub>n</sub>CH<sub>2</sub>-, where n is an integer from 4 to 6, these substituted styrene polymers having an average molecular weight within the range from about 3,000 to about 20,000; and the concentration of component (D) as a percentage of the total composition has a ratio to the concentration of component (A) as a percentage of the total composition that is within a range from about 0.90:1.0 to about 1.6:1.0; and the concentration of component (D) is at least about 0.40 %.

6. A process according to claim 5, wherein, in the liquid composition coated in step (I): the concentration of component (A) is at least about 0.040 M/kg; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is at least about 0.60:1.0 but not greater than about 1.4:1.0; the concentration of component (C) is at least about 0.050 M/kg; component (D) is selected from the group consisting of polymers and copolymers of one or more  $\gamma$ -(N-R<sup>1</sup>-N-R<sup>2</sup>-aminomethyl)-4-hydroxy-styrenes, where  $\gamma$  = 2, 3, 5, or 6, R<sup>1</sup> represents a methyl group, and R<sup>2</sup> represents a substituent group conforming to the general formula H(CHOH)<sub>n</sub>CH<sub>2</sub>-, where n is an integer from 4 to 6, these substituted styrene polymers having an average molecular weight within the range from about 3,000 to about 20,000; the concentration of component (D) as a percentage of the total composition has a ratio to the concentration of component (A) as a percentage of the total composition that is within a range from about 1.05:1.0 to about 1.5:1.0; and the concentration of component (D) is at least about 0.60 % of the total composition.

7. A process according to claim 6, wherein, in the liquid composition coated in step (I): the concentration of component (A) is at least about 0.045 M/kg; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is at least about 0.70:1.0 but not greater than about 1.4:1.0; the concentration of component (C) is at least about 0.055 M/kg; the concentration of component (D) as a percentage of

the total composition has a ratio to the concentration of component (A) as a percentage of the total composition that is within a range from about 1.05:1.0 to about 1.5:1.0; and the concentration of component (D) is at least about 0.80 % of the total composition.

8. A process according to claim 7, wherein, in the liquid composition coated in step  
5 (I): the concentration of component (A) is at least about 0.050 M/kg; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is at least about 0.80:1.0 but not greater than about 1.4:1.0; the concentration of component (C) is at least about 0.060 M/kg; the concentration of component (D) as a percentage of the total composition has a ratio to the concentration of component (A) as a percentage  
10 of the total composition that is within a range from about 1.10:1.0 to about 1.5:1.0; and the concentration of component (D) is at least about 1.00 % of the total composition.

9. A process according to claim 8, wherein, in the liquid composition coated in step (I): the concentration of component (A) is at least about 0.055 M/kg; the ratio of the concentration of component (B) in M/kg to the concentration of component (A) in M/kg is  
15 at least about 0.90:1.0 but not greater than about 1.2:1.0; the concentration of component (C) is at least about 0.064 M/kg; the concentration of component (D) as a percentage of the total composition has a ratio to the concentration of component (A) as a percentage of the total composition that is within a range from about 1.15:1.0 to about 1.3:1.0; and the concentration of component (D) is at least about 1.20 % of the total composition.

20 10. A process according to claim 9, wherein, in the liquid composition coated in step (I): component (A) is fluorotitanate anions; component (B) is divalent manganese ions; component (C) is supplied by addition of orthophosphoric acid to the composition; and there is a pH value from about 2.20 to about 2.70.

11. A process according to claim 10, in which the initial protective coating is a chromate conversion coating.  
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12. A process according to claim 9, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one  
30 of fluorotitanate and fluoro-zirconate.

13. A process according to claim 8, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
14. A process according to claim 7, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
15. A process according to claim 6, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
16. A process according to claim 5, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
17. A process according to claim 4, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
18. A process according to claim 3, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.



19. A process according to claim 2, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
- 5
20. A process according to claim 1, in which the initial protective coating is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorotitanate and fluoro-zirconate.
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/07316

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 7/14

US CL :427/258, 287, 388.4

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/258, 287, 388.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,427,632 A (DOLAN) 27 June 1995 27-06-95), see abstract, column 2, lines 6-65.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

07 MAY 1998

Date of mailing of the international search report

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